Nanocomposites of *in-situ* polymerized Cyclic Butylene Terephthalate and Polyhedral Oligomeric Silsesquioxanes

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Nanocomposites were prepared by in-situ polymerization of CBT®, a cyclic form of poly(butylene terephthalate) (PBT) and polyhedral oligomeric silsesquioxane (POSS®) with 2.5, 5 and 10 wt% POSS content. Three different types of POSS were used; two with reactive functional groups, Trisilanolphenyl POSS (T-POSS) and Glycidyl POSS (G-POSS) and one POSS type having non-reactive functionality, Isooctyl POSS (I-POSS). SEM analysis showed that I-POSS was finely dispersed at a nanoscale level within the CBT, whereas T-POSS and G-POSS formed agglomerates microscaled rather than nanoscaled. T-POSS hinders the polymerization reaction of the CBT, resulting in a poor consolidation of the composite. However, Glycidyl POSS was found to crosslink the CBT during polymerization, making it possible to alter the final material properties. All nanocomposites with 10 wt% POSS content showed a hindered cold crystallization and subsequently showed no melting peak of the formed polymer in a DSC scan.

Introduction

Cyclic butylene terephthalate oligomers as well as polyhedral oligomeric silsesquioxane were commercialized recently. Molten CBT oligomers exhibit a very low, water-like viscosity. They polymerize in an athermal ring-opening polymerization (ROP) into linear poly(butylene terephthalate) (PBT). The polymerization can be performed above as well below the melting temperature of PBT (T_m = 225ºC), making isothermal processing possible [a, d]. POSS molecules on the other hand are a new class of nanomaterial, possessing a cage-like structure made up from silicone and oxygen atoms. The corners of these cages can carry a wide range of funcional groups. These funcional groups determine the matrix compatibility and the final material properties [b, c].

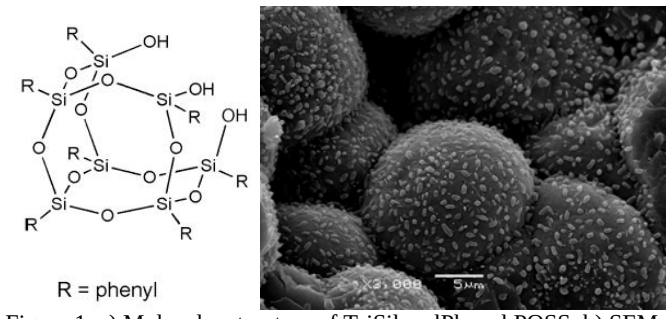

Figure 1. a) Molecular structure of TriSilanolPhenyl POSS, b) SEM micrograph of pCBT/T-POSS

Experimental

Previously dried CBT and POSS were homogenized in a mortar and polymerized in a hot press in ambient atmosphere at 250ºC for 20 min. The polymerized CBT (pCBT) was then cooled in the cold stage of the hot press. Samples were fractured at room temperature, SEM micrographs are shown in fig. 1. Neat CBT and CBT/POSS nanocomposites were in-situ polymerized during the first heating run of a DSC scan (fig. 2). The CBT oligomers melt in the range of 120ºC to 160ºC and subsequently polymerize. The ROP is athermic and therefore can not be detected by the DSC. However, the cold crystallization of the polymerized CBT (pCBT) can be observed in the range of 170ºC to 215ºC. CBT/T-POSS nanocomposites at all studied weight percentages did not show a cold crystallization and as a consequence showed no polymer melting. This hindered cold crystallization was also found for nanocomposites containing G- and I-POSS at 10 wt%, respectively.

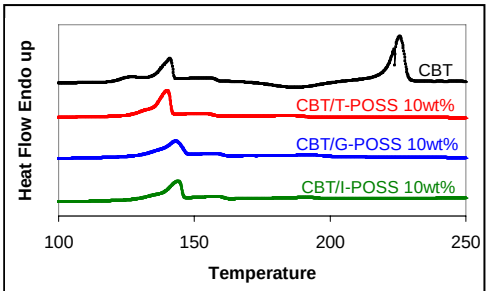

Figure 2. DSC thermograms of CBT and CBT/POSS nanocomposites

Conclusions

- High amounts of POSS hinder the cold crystallization.
- T-POSS and G-POSS agglomerate, whereas I-POSS is finely dispersed in the matrix even at 10 wt%.
- T-POSS interferes with ring-opening polymerization which results in a poorly consolidated material
- G-POSS is a crosslinker and chain extender
- I-POSS shows phase separation, but a small amount of the POSS is finely dispersed at a nanoscale level in the matrix. The excessive I-POSS migrates to the surface of the pCBT sample.

The authors gratefully acknowledge financial support of the Ministerio de Ciencia e Innovación for the projects LIGHTCARBONCARS PSE-370100-2007-1 and PSS-37100-2008-13.

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